DEVELOPMENT OF A BLIND REFERENCE SEDIMENT FOR USE IN UPPER MISSISSIPPI RIVER AND OTHER SEDIMENT QUALITY STUDIES

by

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LIST OF TABLES

ABSTRACT

The Upper Mississippi River has a history of abuse and neglect by Man, resulting in the past contamination of its sediments by heavy metals and organic compounds which were toxic or which bioaccumulated in its aquatic foodchain. Contaminated sediments remain buried today at varying depths in its backwaters and navigation pools. Federal and state biologists involved in the review of sediment dredging projects along the river are therefore routinely required to assess the contaminant implications of those projects to fish and wildlife. That assessment requires a degree of confidence in project-related sediment chemistry data generated by commercial laboratories which has proven to be unwarranted in a number of cases. In some cases, no quality assurance data are provided with analytical results. In other cases, the results have been clearly inaccurate in spite of accurately reported values for National Bureau of Standards reference sediment. In order to be able to attach some estimate of reliability to the data being evaluated for project-related impacts, the team developed its own blind reference sediment from Lake Pepin lakebed material. Nine commercial, one Federal and four state/university analytical laboratories were involved in the development of certified values for 16 heavy metals, DDE, total PCBs, and total organic carbon. The reference material, in wet form, has been used productively for a variety of projects involving the movement of riverine or lakebed sediments. A limited amount of the material can be made available to others facing similar issues.

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INTRODUCTION

The Upper Mississippi River drains an intensively farmed and heavily industrialized watershed. For more than 100 years, unwise agricultural and urban land use practices resulted in an ever increasing loading rate of nutrients and watershed soils to the river. Industrial and domestic developments centered principally around the Minneapolis-St. Paul ("Twin Cities") metropolitan area contributed increasing volumes of eroded upland soils, nutrients, organic and inorganic contaminants to the river system beginning in the late 1800s. Many of those contaminants - including industrial metals and PCBs - became adsorbed onto fine organic and inorganic suspended sediments and were transported downstream. Construction of a series of navigation pools along the river in the late 1930s and 1940s accelerated the deposition of sediments into newly formed backwater areas and has continued to diminish the area and depth of those high-value fish and wildlife habitats.

Dating and chemical analysis of sediment cores obtained from Lake Pepin, a natural riverine lake located approximately 75 miles downstream of the Twin Cities metropolitan area, showed that metal concentrations in sediments deposited in the lake were relatively low before the 1950s, peaked during the early 1970s, and then began to decrease in the late 1970s (Rada et al. 1990). Similar trends in PCB sediment concentrations were found in Lake Pepin and Pool 2 immediately downstream of the Twin Cities (J. Wiener, U.S. Fish and Wildlife Service, LaCrosse, Wisconsin, unpublished data). Similar contaminant deposition patterns are believed to exist within riverine deposition zones (navigation pools and backwaters) upstream and downstream of Lake Pepin.

The Mississippi River has a long history of navigation-related dredging. Initially that dredging consisted primarily of navigation channel maintenance, where the material being dredged was largely riverine sand holding relatively minor amounts of chemical contamination. With passage of Public Law 99-662 in

1986, however, the U.S. Army Corps of Engineers (Corps) was given the authority to construct fish and wildlife habitat rehabilitation and enhancement projects (HREP projects) on the river. Such projects typically involve dredging to deepen backwater areas which have become choked with silt due to riverine impoundment. The Service and other project review agencies have been concerned that contaminated sediments may lie buried at varying depths within those backwaters, especially in areas immediately downstream of major source inputs.

In order to ensure that proposed HREP and other similar dredging projects do not expose fish and wildlife to heavily contaminated sediment strata, planning for such projects requires the collection and chemical analysis of sediment core samples at proposed project sites. Unfortunately, however, the Corps' contract analytical program has not been geared toward effectively verifying analytical quality assurance/quality control. Past experience had shown that some Corps contractors either reported no quality assurance data with their results, or they recognized National Bureau of Standards (NBS) analytical reference materials and reported the corresponding values with considerable accuracy while reporting project sample results which were obviously inaccurate. Similar experiences with NBS reference materials have been reported (Richus 1984). As a result, participating project review agencies - including the Corps' St. Paul District - viewed such reported analytical data as suspect. The goal of the present study was, therefore, to obtain and chemically characterize a substantial volume of Mississippi River sediment for use as true blind riverine reference material in future construction-related sediment quality analyses performed by private laboratories for the Corps and other dredging proponents. Having reliable reference sediment material which could be submitted as a matter of routine along with project-related samples would add a large measure of confidence to review team decisions concerning project-related impacts and/or the possible need for additional toxicity or bioaccumulation testing.

METHODS

In May 1991, personnel from the Corps of Engineers (St. Paul and Rock Island Districts), the Minnesota Pollution Control Agency, the Wisconsin Department of Natural Resources, and the Fish and Wildlife Service's Twin Cities Ecological Services Field Office (TCFO) participated in the collection of approximately sixty gallons of candidate reference sediment from an area of lower Lake Pepin known to be enriched with heavy metals and PCBs. After establishing starting point latitude and longitude with LORAN C, the sediment was collected by placing consecutive petite ponar grabs obtained along a west-to-east transect into six randomly assigned, chemically clean, stainless steel 10-gallon containers. When filled, the containers were taken to the LaCrosse National Fisheries Research Center and refrigerated overnight. The following day, the containers were randomly paired for mixing as 20-gallon batches in a large Hobart blender. After approximately 25 minutes of mixing, each batch was immediately portioned into individual chemically clean glass containers, identified as Sample 1, 2, or 3 and frozen. Sediment samples from each of the three batches were submitted to 14 laboratories for heavy metal, organochlorine/PCB (OC/PCB), total organic carbon (TOC), or grain size determinations (Table 1).

Upon completion of analyses, all results were sent to the Patuxent Analytical Control Facility, U.S. Fish and Wildlife Service, for processing. Results were entered into a Lotus 123 spreadsheet, and the raw comparative data was printed and sent to the participating laboratories for review for discrepancies.

The certified value for each parameter was established by taking a mean of the laboratory means of reasonably similar results. Certifications were not made unless the results of at least three laboratories could be included in the mean value calculation. Data points were determined to be "outliers" if they differed from the calculated mean by more than two standard deviations.

RESULTS AND DISCUSSION

Table 2 contains the certified values determined for selected parameters in the Lake Pepin blind reference sediment. Included for each parameter is the mean value, standard deviation, and number of data sets used to compute the mean.

Few organochlorine compounds were determined to be present. Those which were found were at concentrations near the limit of detection for most routine analytical methods. Only total PCBs (0.23 ppm) and p,p'-DDE (0.016 ppm) were present at sufficiently high concentrations and frequency for certification. Metals concentrations were higher and, in most cases, order of magnitude certifications were possible. Analysis of metals data was complicated by the variety of digestions used by participating laboratories. Most participants appeared to have used strong acid digestions, such as hydrochloric or nitric acid or mixtures of the two. Several laboratories appear to have used even stronger digestions (hydrofluoric acid) to completely dissolve the sediment. While both techniques are widely used, the results for some elements (eg. aluminum, barium, cadmium, manganese, nickel, lead) are not directly comparable. Where it appeared that a stronger digestion method affected the results, the higher values obtained were not used in the certification. There were insufficient data to allow certification for methods which used hydrofluoric acid. In interpreting laboratory performance on the basis of Lake Pepin reference sediment, it is essential that the digestion method be known. Laboratories using complete (hydrofluoric acid) digestions should generally obtain higher results than those identified in Table 2.

Total organic carbon in the reference sediment was measured by several laboratories and its mean value is included in Table 2. While selected laboratories also were asked to determine grain size as percent sand, silt and clay, the differing reporting formats and extremely variable results made certification impossible. Qualitatively, the material resembles a very fine, dark, organic silt.

CONCLUSIONS

While the stability of the wet Lake Pepin blind reference sediment has not been established, most of the certified analytes are expected to remain stable for many years under storage at -20 degrees centigrade. TCFO intends to submit at least one sample to the Patuxent Analytical Control Facility every two to three years to verify stability of the remaining reference material.

The reference sediment has proved useful in a number of situations to-date. TCFO has required analysis of the material by private and municipal dredging proponents in conjunction with its review of several Corps Section 10 and Section 404 dredge and fill permits on the Upper Mississippi River. TCFO has also incorporated analysis of the material into its requests for additional sampling and analysis of wetland soils at two Superfund sites. The St. Paul District Corps has used the material both to screen candidate laboratories for multi-project analytical contract awards and as a quality check for individual HREP project analyses. The Wisconsin Department of Natural Resources is considering its use as a sediment analysis screening tool in its private laboratory certification program. The Minnesota Pollution Control Agency has required its analysis in municipal permits involving sediment testing, in quality assurance checks for its own contract laboratories, and in its reviews of other projects involving the movement of sediments.

TCFO is willing to share limited quantities of the above reference sediment with Field Offices facing similar laboratory quality assurance issues. Users should specify the digestion method for metals analysis or, at minimum, require that the method used be reported with the results. Confidence intervals that meet the user's individual needs can be computed. Our only request is that a shipping container be provided, and return shipping expenses be paid, by the user. We strongly support the initiation of similar efforts by others to develop reference sediment material containing differing analyte proportions and concentrations, and would urge the sharing of that material with other Contaminants Program personnel.

TABLES

Table 1. Laboratories where sediment samples were submitted for select analytes.

Laboratory	Analyte
Environmental Trace Substances Research Center, Columbia, MO	metals
Geological and Environmental Research Group, Texas A&M, College Station, TX	OC/PCBs, TOC grain size
Hazleton Laboratories America, Inc, Madison, WI	metals, OC/PCBs
Mississippi State Chemical Laboratory, Mississippi State, MS	OC/PCBs
Research Triangle Institute, Research Triangle Park, NC	metals
Patuxent Analytical Control Facility, Laurel, MD	metals, OC/PCBs
Applied Research and Development Laboratory, Mount Vernon, IL	metals, PCBs, TOC, grain size
Hazleton Environmental Services, Madison, WI	metals, PCBs, TOC grain size
SERCO Laboratories, St. Paul, MN	metals, PCBs, TOC, grain size
Twin City Testing Corporation, St. Paul, MN	metals, PCBs, TOC, grain size
Minnesota Dept. of Health, St. Paul, MN	metals, OC/PCBs,
CTRC, University of Minnesota, Duluth, MN	PCBs
State Laboratory of Hygiene, University of Wisconsin, Madison, WI	metals, PCBs, TOC
University of Wisconsin Extension, Soil and Plant Analysis Laboratory, Madison, WI	grain size

Table 2   Certified dry weight values for Lake Pepin blind reference sediment.

Analyte	Concentration (PPM, Dry Wt.)	Standard Deviation	Number of Laboratories
Metals[a]			
Aluminum	16000	6600	3
Boron	21	3.0	3
Barium	270	3.0	3
Beryllium	1.2	0.43	5
Cadmium	3.6	0.69	7
Chromium	56	6.7	5
Copper	41	3.8	8
Iron	40000	12000	5
Lead	54	11	7
Mercury	0.24	0.067	9
Magnesium	9200	1600	4
Mangenese	2300	220	5
Nickel	34	3.8	7
Strontium	47	1.9	3
Vanadium	47	29	4
Zinc	180	26	8
Organics			
p,p'-DDE	0.016	0.009	3
Total PCB	0.23	0.12	9
Total Organic Carbon			
TOC	3.2	0.99	6

Stong acid digestion (not complete dissolution).

REFERENCES

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